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RECOVERY OF THE ELECTRICAL RESISTIVITY IN VARIOUS TYPES OF PYROLYTIC CARBON AFTER NEUTRON IRRADIATION AT - 196° C

M. DOMENICI, U. PERITO, F. PIERAGOSTINI, H. WALTHER

Paper presented at the «2nd CONFERENCE ON INDUSTRIAL CARBON AND GRAPHITE», London, April 1965

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RECOVERY OF THE ELECTRICAL RESISTIVITY IN VARIOUS TYPES OF PYROLYTIC CARBON AFTER NEUTRON IRRADIATION AT -196°C

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1. INTRODUCTION

In the recent years a number of experimental [1,2,3,4,5] and theoretical [6,7] works has been devoted to the study of recovery of radiation damage in graphite, irradiated at low temperature.

Also pyrolytic carbon (P.C.) has received increasing attention in this field [8,9,10], mainly because of the particular characteristics which make it suitable for various technical applications, and of the interest for its structure which can have a very wide range in its degree of graphitization [11,12,13].

Up to now, neither the theoretical investigations, which in some instances are well self-consistent, have obtained a satisfactory confirmation by experimental work, nor the large amount of data available on the annealing of physical parameters investigated give rise to a complete picture of the recovery processes.

As part of a more general program on pyrolytic carbon in progress at our laboratories, we report here the radiation damage work, whose particular aim is to contribute to a better understanding of the recovery mechanism of the defects introduced by irradiation, and their relative influence on the properties of the pyrolytic carbon.

This part is developed by observing the behaviour of different physical parameters and by submitting the irradiated samples to both isochronal and isothermal annealing, in order to derive information on the type of the defects and their relative kinetics in the various annealing stages.

Previous results have been reported in ref. [14] dealing with the isochronal annealing of electrical resistivity, c-spacing and preferred orientation on different types of P.C.

In the present work the above mentioned study has been continued also by isothermal annealing of the electrical resistivity and more information have been gained about the process.

2. EXPERIMENTAL

In Table I we have collected the characteristics of the samples (50 x 5 x 3 mm in size) employed in this research, and irradiated at -196°C in two runs at neutron doses of 1.42×10^{18} and 6.85×10^{17} n/cm^2 (E > 1 MeV).

More detailed information on the physical characteristics of the samples and on the irradiation facility can be found in [14].

The electrical resistivity measurements parallel to the deposition plane have been carried out before and after irradiation, at the base temperature of liquid nitrogen utilizing a usual potentiometric system with a reference sample as standard.

Electrical contacts were realized by an electrolytic silver deposition at both ends of the samples; to each one two suitable terminals of copper wire were welded. With this type of contacts, the reproducibility of the resistivity measurements was estimated to be ± 0.2%.

The isothermal annealing curves were measured after the isochronal ones and the samples utilized for the experiments here reported, were stored in liquid nitrogen for some weeks.

The specific resistivity variations $\frac{\Delta\rho}{\rho_o}$ were calculated by the formula

$$\frac{\Delta\rho}{\rho_o} = \frac{R-R_o}{R_o} \qquad (1)$$

where R is the resistance of the specimen after each thermal treatment; R_o and ρ_o are respectively the resistance and the resistivity (at -196°C) of the sample before irradiation.

To give results also in a normalized form, the fraction of extra resistivity has been calculated by the ratio $f = \Delta\rho/\overline{\Delta\rho}$, being $\overline{\Delta\rho}$ the increase of resistivity after irradiation, before any annealing.

Annealing treatments were performed by using proper liquid stirred baths: propane, between -190°C and -90°C; ethanol, between -90°C and room temperature; silicon oil, beyond.

The temperature of the baths, measured by a Leeds & Northrup platinum resistance thermometer, was maintained constant during each treatment with an accuracy of ± 0.25°C.

3. RESULTS

3.1. Analysis of the recovery stages

In Fig. 1 some results of our previous work [14], dealing with isochronal annealing, are reported.

They are presented in a differential form and the absolute values of $\frac{df}{dT}$ ($°C^{-1}$) versus annealing temperature T are given for four types of P.C., coming from four different high temperature treatments (HTT) before irradiation. Two samples for each type have been considered (see Table I for identification).

In this figure, the series of experimental points ($f = \Delta\rho/\overline{\Delta\rho}$) vs. T are also indicated for only a curve of each type, as an example. All the isochronal curves shown here were obtained by annealing pulses of 10 min at each annealing temperature.

From an examination of these differential curves, it appears that:

1) It is possible to identify, in the explored temperature range, three well defined intervals of temperature, in which the recovery of the neutron induced extra-resistivity takes place for all the examined samples. We have indicated at the top of Fig. 1 these three stages as I_n-1, I_n-2 and I_n-3, covering respectively the intervals -190 to -140°C; -140 to -20°C and -20 to +50°C. This conventional denomination, suggested by the experience of previous work [15], takes into account the fact that, in contrast with the case of many metals, no electrical resistivity recovery (either for graphite or for P.C.) has been observed below liquid nitrogen temperature [3, 5].

2) Assuming this scheme, it can be observed that, for samples with decreasing values of HTT, the peak related to the stage I_n-2 tends to shift vs. lower annealing temperature, whilst the I_n-3 peak tends to desappear and the I_n-1 peak tends to decompose into two peaks, where the second one, centered at a higher annealing temperature, survives for the sample heat treated at 2000°C.

Such effects will be discussed later in detail.

3.2. Isothermal annealing

Starting from the above described analysis, some samples of type A II, B II and D II, irradiated at the lower dose of 6.85×10^{17} n/cm^2, were submitted to isothermal annealing around the temperature to which the maximum for each stage is registered.

In the case of sample D II a further isothermal annealing has been carried out at -80°C, where the residual peak of stage I_n-3 has been tentatively individuated.

The obtained results are shown in Fig. 2, in which the annealing temperatures are indicated together with the sample types, with reference to Table I.

These results were employed to deduce the activation energies of the processes involved in any single stage, by means of the method of Meechan and Brinkman [16], that is by comparison with the corresponding isochronal curves.

The values of activation energies so derived are shown by the plots of Fig. 3 following the order of the stages.

The obtained values are for stage I_n-1 0.20 eV; for stage I_n-2 between 0.68 and 0.84 eV; and for stage I_n-3 between 0.82 and 0.90 eV, as summarized in Table II. Most of them refer to isochronal curves taken with 10 min steps, other ones refer to 1 min steps and are indicated by (*) in Table II; all refer however to samples irradiated at the same dose.

4. DISCUSSION

As in the annealing process three well defined stages appear (section 3.1.), these stages may be discussed separately in order to derive the respective interpretations.

4.1. Stage I_n-1

The observed increase of electrical resistivity, c-spacing and preferred orientation has suggested, as described in our former work [14], a clustering process of moving interstitial type defects in this temperature range. This has been supported mainly by the reasonable assumption, already made by Kinchin [17], that clusters of interstitial type defects have a greater effect on c-spacing than the same number of separate single defects. The increase in electrical resistivity should be attributed in this case to an increase in electron scattering power.

An analogous clustering process in graphite has been predicted by the theory of Iwata and Suzuki [6], but for temperatures below that of the liquid nitrogen, as the calculation of the activation energy gave the low value of 0.016eV.

Such clusters described by these authors are atomic ones, where the stable interatomic distances are about 10 Å. Our interpretation may agree with the formation of "atomic clusters" but the temperatures where it occurs must be just above that of the liquid nitrogen, since it has been generally observed, that no remarkable resistivity annealing occurs below this temperature [3], [5].

The isothermal annealing plot in stage I_n-1 seems to demonstrate that, for the sample (HTT 3000°C) examined at -170°C (unfortunately only one), the process is mono-ac-

tivated. The deduced activation energy of 0.20 eV has to be compared - as far as the case of P.C. can be related to the case of graphite - with the lower value of about 0.07 eV reported by Schweitzer [7], as well as with the higher ones of 0.5 eV (for free interstitial motion) and 0.31 eV (for interstitial motion in the neighborhood of a repelling vacancy) reported by Goggin and Reynolds [4].

The peak position of stage I_n-1 depends (as already anticipated in 3.1.) on the foregoing heat treatment of the sample, a feature which is even more evident for stage I_n-2 and will be discussed in 4.2.

Concerning the peak height, it can be observed that it appeared dose dependent. The greater dose gave a lower peak height, as observed also by other authors [3],[4]. An interpretation could tentatively be seen in a mechanism according to which the higher concentration of interstitials at higher doses gave already rise to some clusters, where the knock-on atoms during their slowing down processes would be the moving particles. Therefore one part of the anomalous resistivity increase would have taken place already during irradiation.

4.2. Stage I_n-2

This stage is characterized by a rapid decrease in electrical resistivity, the c-spacing however does not yet decrease [14].

Any process which would result in a complete declustering of interstitials cannot serve therefore as a satisfactory interpretation, as long as the c-spacing variation is attributed to a clustering.

The theory of Iwata and Suzuki predicts a second mechanism following their first one, which consists in the formation of C_2-molecules from the foregoing atomic clusters.

This should take place however at about -170°C, having a calculated value of potential barrier of about 0.6 eV for the formation of C_2-molecules. Our results for stage I_n-2 may agree also with this second mechanism but not (as for stage I_n-1) with the indicated temperature range where it should take place. In fact, accepting this process a decrease in c-spacing is not to be assumed, since the C_2-molecules would occupy the same zones as formerly the atomic clusters. On the other hand, the approach of two interstitials beyond a certain distance would reduce their scattering power for electrons, and explain the decrease in electrical resistivity.

The activation energies we have deduced for all the samples, although the isothermal curves do not seem to be mono-activated, range between 0.68 and 0.84 eV, and agree sufficiently with the calculated potential barrier of 0.6 eV.

At the temperatures of I_n-2, Bochirol et al. [18] observed a peak of stored energy release denominated "E" peak.

The position of the peak in stage I_n-2 shows with good evidence the dependence of the annealing process on the structural characteristics of the samples.

In fact, the shift observed when passing from more graphitized to less graphitized samples shows a transition with sample HTT 2500°C (Fig. 1, in which the results refer to two samples irradiated with the same dose). This evi-

dence can be related to the existence of a transition point from bidimensional to three-dimensional layer order in the samples, as already pointed out [9] for many physical properties of P.C.

In Fig. 4 the temperature values corresponding to the peak-maximum of I_n-1, I_n-2 and I_n-3 have been plotted versus heat treatment temperature together with the initial values of electrical resistivity ρ_o, to give a better evidence of this phenomenon.

4.3. Stage I_n-3

The existence of this stage, appearing after the rapid recovery of electrical resistivity of stage I_n-2 in the isochronal curves, is accompanied by an initial very low decrease of c-spacing [14]; it results much more evident in the differential plots, from which also the influence of both dose and structure can be deduced.

Concerning the structure dependence, Fig. 4 shows that the temperature of annealing, at which the maximum of the peak is registered, tends to shift to lower values, if it is assumed that the shoulders around -80°C are the residuals of this peak for samples HTT 2500°C and HTT 2000°C (Fig. 1).

The activation energy values between 0.82 and 0.9 eV derived with the aid of the isothermal curves (Fig. 2, which seem to be not in all cases mono-activated), suggest that the free motion of di-interstitials (or C_2-molecules), formed in the previous stage, is responsible of the present stage of annealing.

This interpretation is consistent with the results of Goggin [19] on the annealing of Young's modulus of graphite

after electron irradiation, who found an anomalous peak centered just between the stages I_n-2 and I_n-3. The increase of this peak was related to the formation of double interstitials, in agreement with our deduction in section 4.2 for stage I_n-2; its decrease was related to the motion of di-interstitials and agrees with our interpretation for stage I_n-3.

The activation energy deduced in the mentioned paper is 0.9 eV, well consistent with our values.

We can also recall that Bochirol et al. [18] found a peak of stored energy release around 20°C, denominated "F" peak.

Referring again to the Iwata and Suzuki theory [6], we can compare the present deductions with the third process inferred by these authors, who speak about inclustering of C_2-molecules in a temperature range again lower than stage I_n-3 defined by us. Keeping in mind that the c-spacing begins to decrease slowly, starting from about -20°C [14], we can accept this view as a possible consequence of double-interstitial motion, but cannot reject the cooperative annihilation of interstitial-type defects either with vacancies or at the grain-boundaries, which could already start also in stage I_n-2. This would explain why the present stage is less evident in less graphitized samples, which generally have smaller crystallite dimensions, and why such a rapid decrease of electrical resistivity takes place during these stages.

5. CONCLUSION

The annealing of P.C. following neutron irradiation at liquid nitrogen temperature has been described in this work by means of two series of considerations.

The first one concerns the definition of suitable intervals of temperature identifying each individual process, as well as the relative limits of this picture regarding the influence of the structure of the samples and/or the dose received.

The second one concerns the description of the mechanism, the nature of point-defects and the related activation energies governing the recovery in any single stage.

In more details the following information have been obtained:

a) The process controlling stage I_n-1, associated with an energy of ~0.2 eV, is to be ascribed to the formation of interstitial clusters.

b) Stage I_n-2, controlled by an activation energy of 0.68 ÷ 0.84 eV is to be related mainly to the formation of double interstitials.

c) Migration of double interstitials, possibly to form molecular clusters, takes place in stage I_n-3 with an activation energy of 0.82 ÷ 0.90 eV.

d) Contemporary annihilation of interstitial type defects with vacancies or at the grain-boundaries cannot be ruled out in both stages I_n-2 and I_n-3, especially for less graphitized samples.

The comprehensive picture here described is in agreement

with the theoretical considerations of Iwata and Suzuki [6], concerning the development of a series of successive processes during the annealing from very low temperature, but the activation energies experimentally deduced in our work tend to shift towards higher temperature the occurrence of the single successive processes.

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TABLE I - Summary of experimental data

Specimen	HTT (°C)	Fast neutron dose (E>1MeV) (n/cm^2)	$\overline{\Delta\rho}$ ($10^{-4}\Omega$ cm)	ρ_o(at-196°C) ($10^{-4}\Omega$ cm)	$\overline{\Delta\rho}/\rho_o$	Annealing treatment
A-I 10	3000	$1.42 \cdot 10^{18}$	7.31	0.75	9.69	Ic. 10'
B-I 16	2750	"	4.77	4.24	1.12	Ic. 10'
C-I 21	2500	"	2.49	7.73	0.32	Ic. 10'
C-I 23	2500	"	3.81	5.34	0.71	Ic. 10'
D-I 3	2000	"	1.69	8.63	0.196	Ic. 10'
A-II 70	3000	$6.85 \cdot 10^{17}$	5.34	0.74	7.21	Ic. 10'
A-II 72	3000	"	5.51	0.72	7.65	It.-170°C; It.-50°C; It.+15°C
B-II 61	2750	"	5.26	2.09	2.52	Ic. 10'
B-II 59	2750	"	5.27	1.46	3.61	It.-40°C; It.+5°C
D-II 54	2000	"	0.33	8.44	0.04	Ic. 10'
D-II 57	2000	"	0.71	8.55	0.083	It.-120°C; It.-80°C

Ic. : Isochronal annealing

It. : Isothermal annealing

TABLE II - Activation energies deduced for the three recovery stages

Samples employed in the isothermal experiments	Samples employed in the isochronal [14] experiments	HTT (°C)	Energies (eV)		
			Stage I_n-1	Stage I_n-2	Stage I_n-3
A-II 72	A-II 69	3000	0.20	0.80	0.82
	A-II 70		-	0.80	0.90
B-II 59	B-II 61	2750	-	0.78	0.85
	B-II 64(*)			0.84	0.86
D-II 57	D-II 54	2000	-	-	-
	D-II 53(*)			0.68	0.84

(*) Isochronal curves obtained with annealing pulses of 1 min .

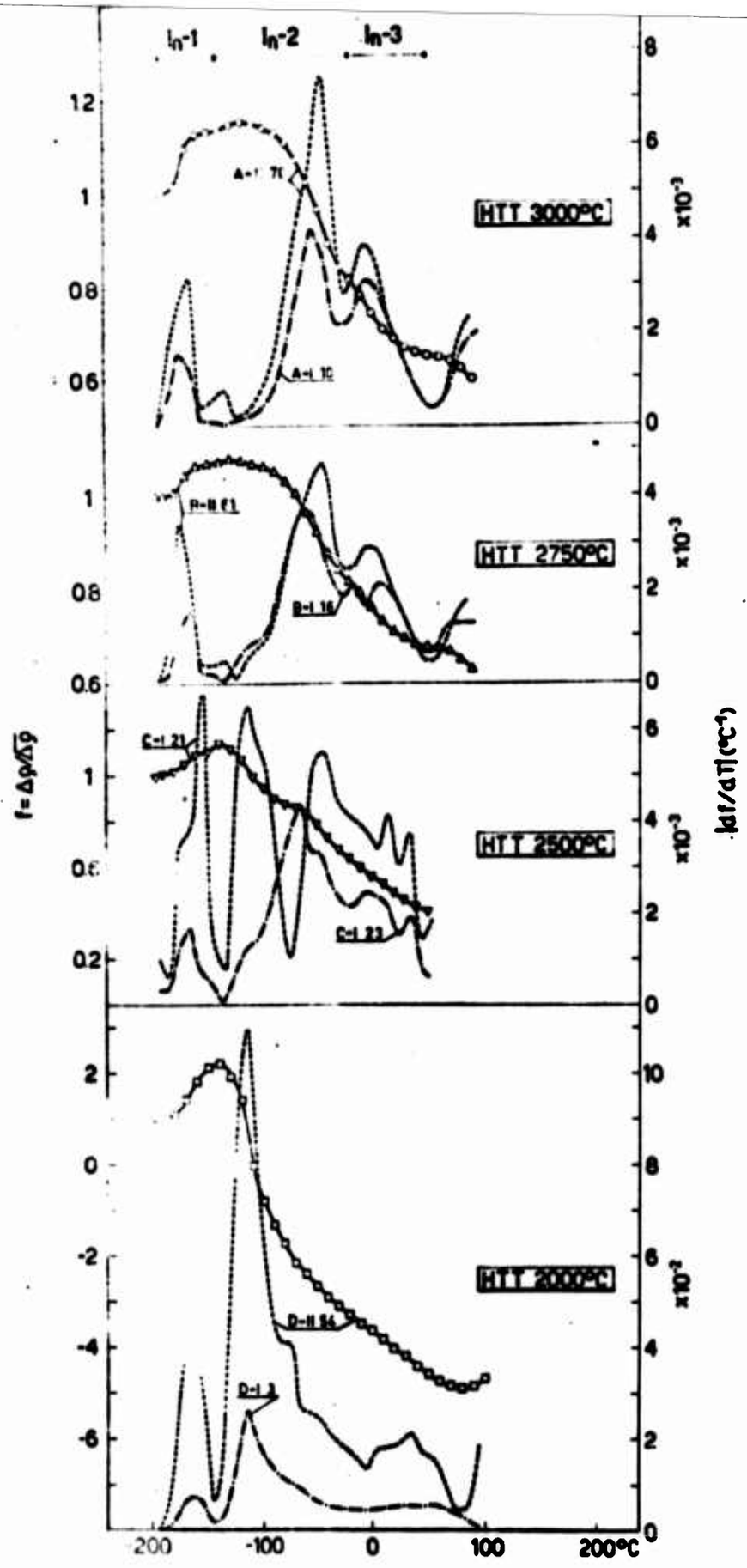

Fig. 1 - Recovery of electrical resistivity of P.C. after neutron irradiation at -196°C, in normalized and differential form (Dose I: $1.42 \cdot 10^{18}$ n/cm^2; dose II: $6.85 \cdot 10^{17}$ n/cm^2).

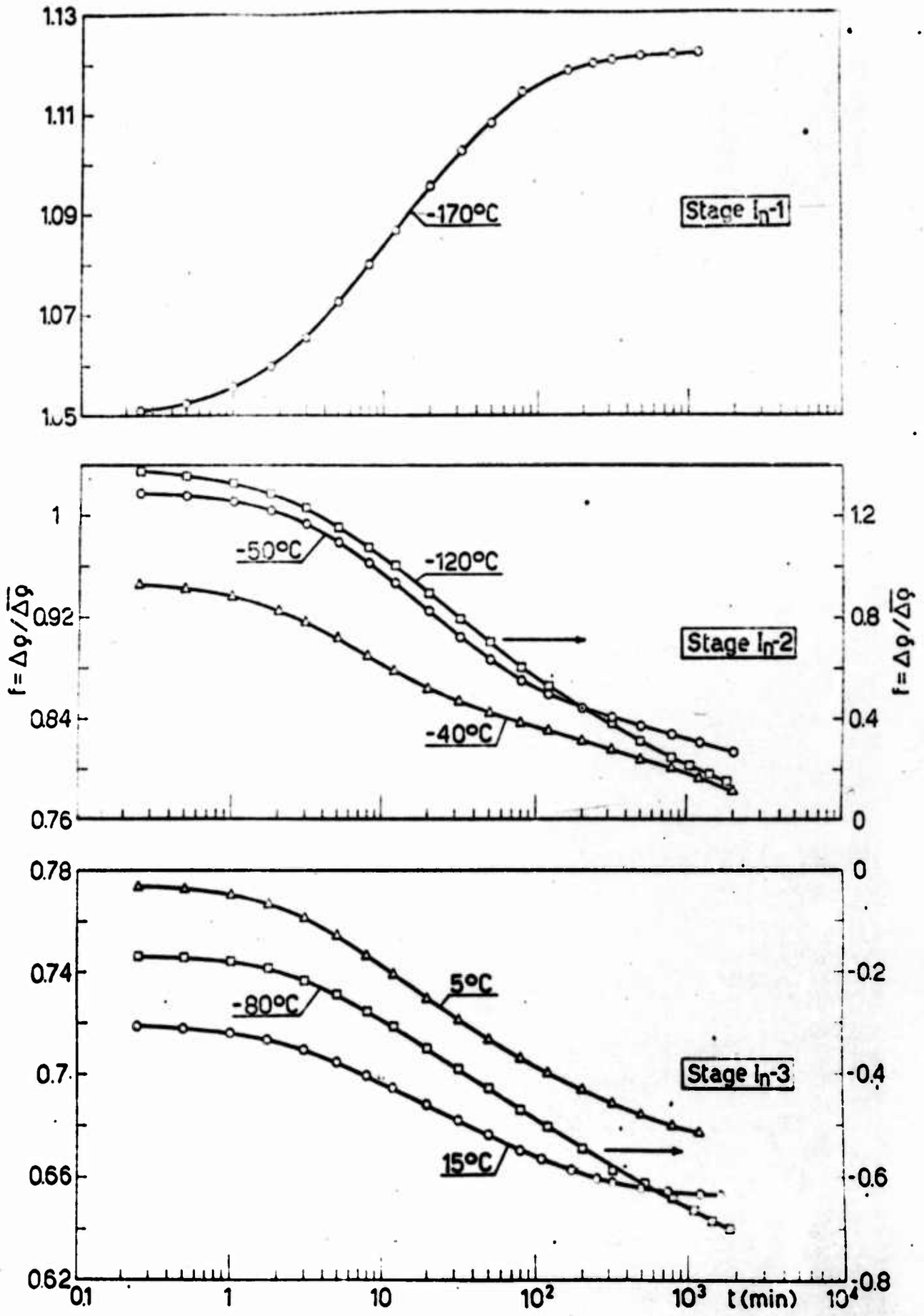

Fig. 2 - Isothermal annealing curves of P.C. HTT 3000°C (-O-O-), HTT 2750°C (-Δ-Δ-) and HTT 2000°C (-□-□-). Dose: $6.85 \cdot 10^{17}$ n/cm^2.

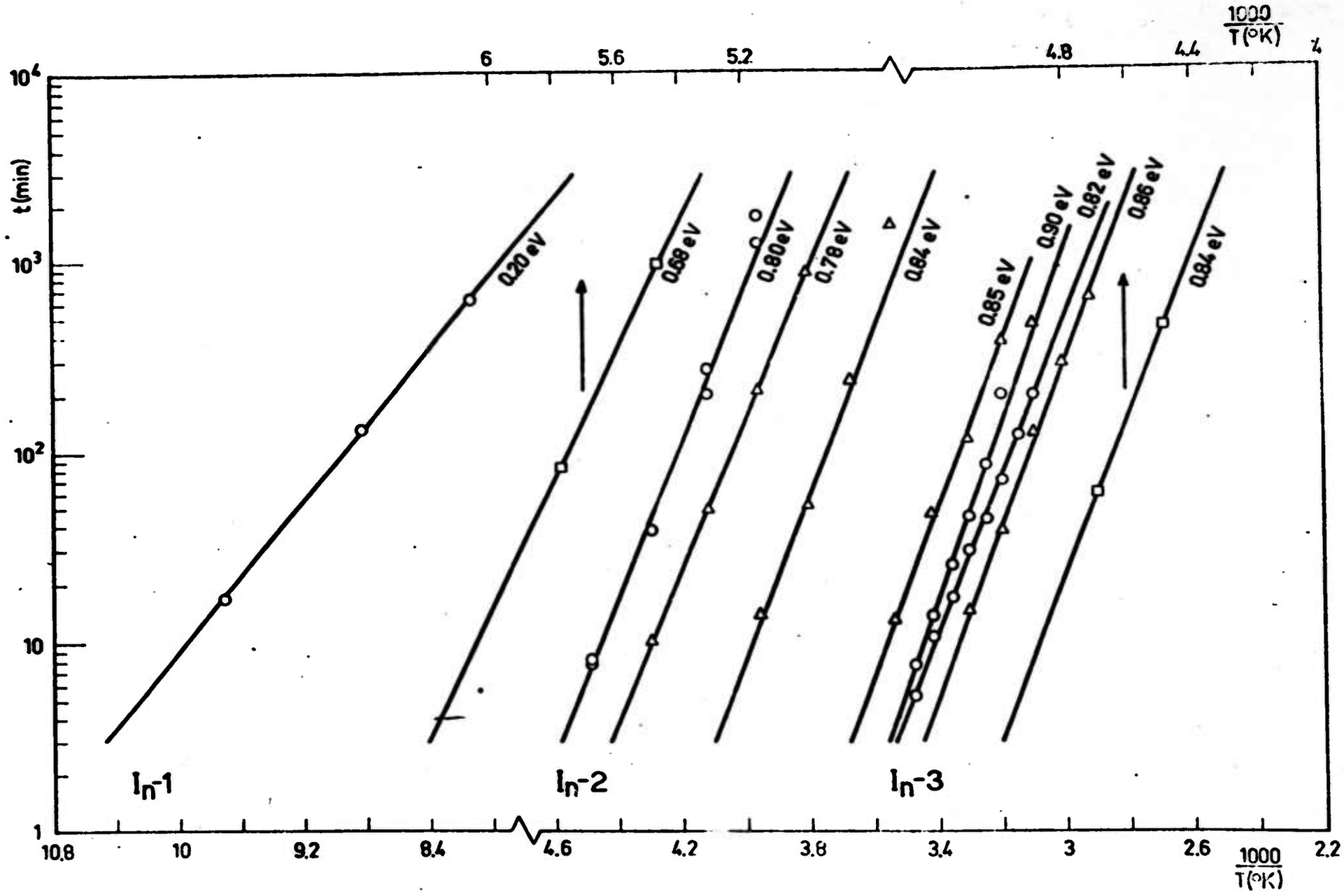

Fig. 3 - Determination of activation energies of stages I_n-1, I_n-2 and I_n-3. (Convention symbols as in Fig. 2).

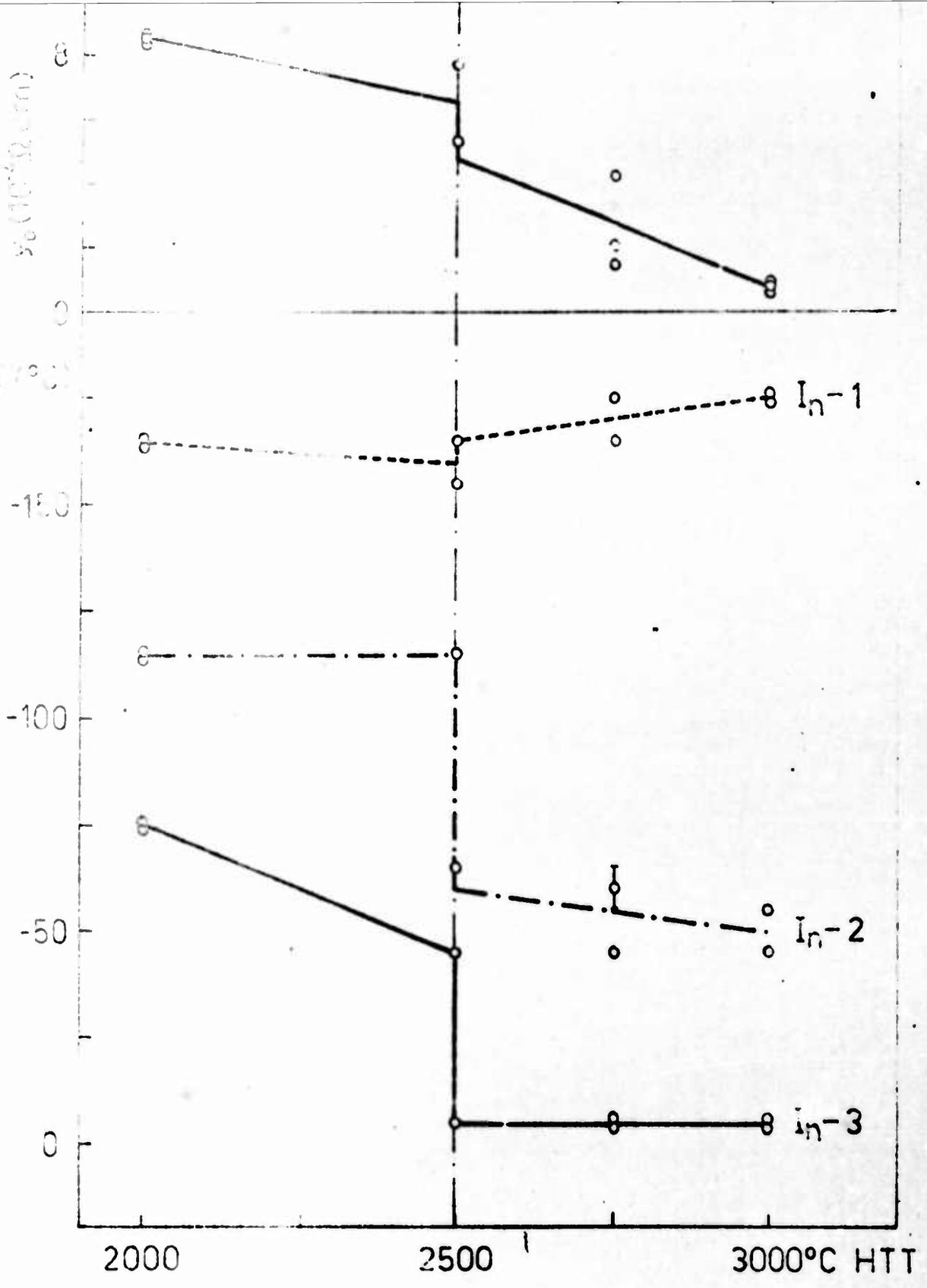

Fig. 4 - Dependence on the sample structure of ρ_o (at -196°C) and of the peak positions for the various stages.